Ruthenium Complexes Containing "Noninnocent" *o*-Benzoquinone Diimine/*o*-Phenylenediamide(2−) Ligands. Synthesis and Crystal Structure of the Nitrido-Bridged Complex $[\{LRu(o\text{-}C_6H_4(NH)_2)\}_2(\mu\text{-}N)](PF_6)_2\cdot 3CH_3CN\cdot C_6H_5CH_3$

Thomas Jüstel,[†] Jesper Bendix,[†,‡] Nils Metzler-Nolte,[†] Thomas Weyhermüller,[†] Bernhard Nuber,[§] and Karl Wieghardt*,[†]

Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34−36, D-45470 Mülheim an der Ruhr, Germany, and Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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Reaction of $LRu^{III}Cl_3$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) with 1,2-phenylenediamine ($opdaH_2$) in H_2O in the presence of air affords $[LRu^{II}(bqdi)(OH_2)](PF_6)$ (**1**), where (bqdi) represents the neutral ligand *o*-benzoquinone diimine. From an alkaline methanol/water mixture of **1** was obtained the dinuclear species $[\{LRu^{II}(bqdi)\}_2(\mu\text{-}H_3O_2)](PF_6)_3$ (**1a**). The coordinated water molecule in **1** is labile and can be readily substituted under appropriate reaction conditions by acetonitrile, yielding $[LRu^{II}(bqdi)(CH_3CN)](PF_6)_2$ (**2**), and by iodide and azide anions, affording $[LRu^{II}(bqdi)I](PF_6)\cdot 0.5H_2O$ (**3**) and $[LRu(bqdi)(N_3)](PF_6)\cdot H_2O$ (**4**), respectively. Heating of solid **4** in vacuum at 160 °C generates N_2 and the dinuclear, nitrido-bridged complex $[\{LRu(o\text{-}C_6H_4(NH)_2)\}_2(\mu\text{-}N)](PF_6)_2$ (**5**). Complex **5** is a mixed-valent, paramagnetic species containing one unpaired electron per dinuclear unit whereas complexes **1**−**4** are diamagnetic. The crystal structures of **1**, **1a**$\cdot 3CH_3CN$, **3**, **4**$\cdot H_2O$, and **5**$\cdot 3CH_3CN\cdot 0.5$(toluene) have been determined by X-ray crystallography: **1** crystallizes in the monoclinic space group $P2_1/m$, $Z = 2$, with $a = 8.412(2)$ Å, $b = 15.562(3)$ Å, $c = 10.025$ Å, and $\beta = 109.89(2)°$; **1a**$\cdot 3CH_3CN$, in the monoclinic space group $C2/c$, $Z = 4$, with $a = 19.858(3)$ Å, $b = 15.483(2)$ Å, $c = 18.192(3)$ Å, and $\beta = 95.95(2)°$; **3**, in the orthorhombic space group *Pnma*, $Z = 4$, with $a = 18.399(4)$ Å, $b = 9.287(2)$ Å, and $c = 12.052(2)$ Å, **4**$\cdot H_2O$, in the monoclinic space group $P2_1/c$, $Z = 4$, with $a = 8.586(1)$ Å, $b = 15.617(3)$ Å, $c = 16.388(5)$ Å, and $\beta = 90.84(2)°$; and **5**$\cdot 3CH_3CN\cdot 0.5$(toluene), in the monoclinic space group $P2_1/c$, $Z = 4$, with $a = 15.003(3)$ Å, $b = 16.253(3)$ Å, $c = 21.196(4)$ Å, and $\beta = 96.78(3)°$. The structural data indicate that in complexes **1**−**4** the neutral *o*-benzoquinone diimine ligand prevails. In contrast, in **5** this ligand has predominantly *o*-phenylenediamide character, which would render **5** formally a mixed-valent $Ru^{IV}Ru^{V}$ species. On the other hand, the Ru−N bond lengths of the Ru−N−Ru moiety at 1.805(5) and 1.767(5) Å are significantly longer than those in other crystallographically characterized $Ru^{IV}{=}N{=}Ru^{IV}$ units (1.72−1.74 Å). It appears that the $C_6H_4(NH)_2$ ligand in **5** is noninnocent and that formal oxidation state assignments to the ligands or metal centers are not possible.

Introduction

The dianionic form of doubly deprotonated *o*-phenylenediamine is probably the archetype "noninnocent" ligand. Its coordination chemistry has attracted the interest of chemists because of the inherent problems associated with the assignment of formal oxidation levels to the metal and the ligand itself in a given transition metal complex.[1] In principle, the ligand can bind as *o*-phenylenediamide(2−), *o*-benzosemiquinone diimide(1−), or neutral *o*-benzoquinone diimine to a transition metal ion (Scheme 1). As Lever et al.[2] have stated, "the electron distribution (in a coordination compound) will depend on the extent of mixing between the metal and ligand orbitals, which, in turn, is a function of the energies, symmetries, and overlap of the valence metal and ligand orbitals."

Conventional wisdom predicts then that the observed (measured) C−N and C−C bond lengths in a given complex containing the coordinated $C_6H_4(NH)_2$ chelate should reflect its oxidation level. Thus two short C−N bonds in conjunction with two short conjugated and four longer C−C bonds in the ring indicate (bqdi) character. In contrast, long C−N bonds and six equivalent C−C bonds in ring are typical of the $(opda)^{2-}$ formulation.

Ruthenium(II) complexes containing a (bqdi) ligand have been synthesized[3] and structurally characterized,[4] e.g. $[Ru^{II}$-

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[†] Max-Planck-Institut.

[‡] On leave from the University of Copenhagen.

[§] Universität Heidelberg.

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(1) See for example the discussion of the bonding in $[Ni(C_6H_4(NH)_2)_2]$: (a) Feigl, F.; Fürth, M. *Monatsh. Chem.* **1927**, *48*, 445. (b) Nyholm, R. S. *Chem. Rev.* **1953**, *53*, 263. (c) Stiefel, E. I.; Waters, J. H.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3016. (d) Balch, A. L.; Holm, R. H. *J. Am. Chem. Soc.* **1966**, *88*, 5201. (e) Swartz Hall, G.; Soderberg, R. H. *Inorg. Chem.* **1968**, *7*, 2300.

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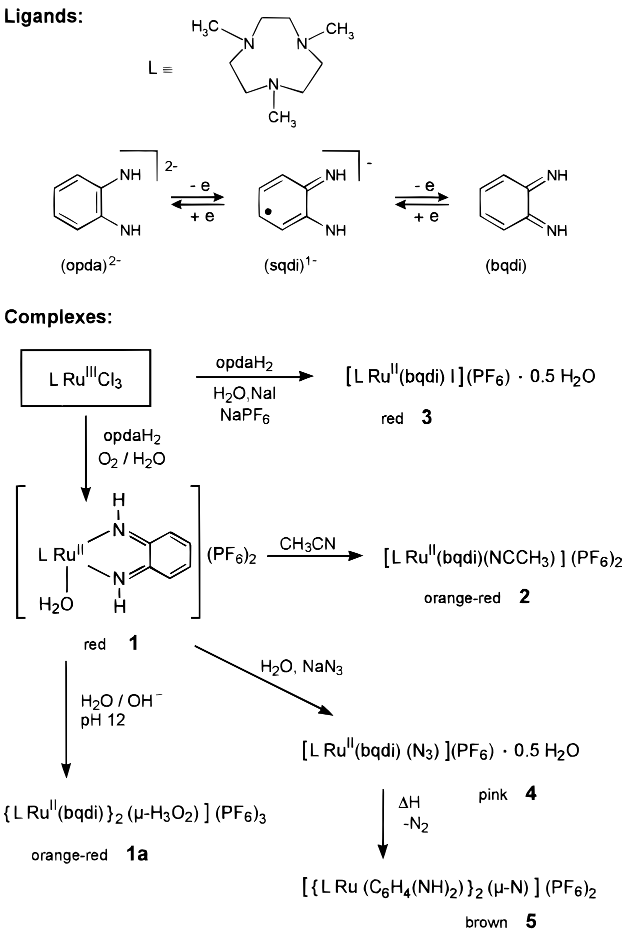
Scheme 1. Ligand Abbreviations and Syntheses of Complexes



$(bpy)_2(bqdi)](PF_6)_2$, where the stability of the (bqdi) ligand has been ascribed to its π-acceptor capability in conjunction with a low-spin Ru^{II} ion as π-donor; an "electron-poor" ligand binds to an "electron-rich" metal center. On the other hand, Wilkinson et al.[5] recently described some rhenium complexes with formally high oxidation states (up to +VII) containing $(opda)^{2-}$ ligands—a combination of an "electron-rich" ligand with an "electron-poor" metal ion. In both papers,[4,5] structural parameters of the above type obtained from X-ray crystal structure determinations were invoked to assign the respective oxidation levels. In all cases, the estimated standard deviations, σ, reported by these authors for the C−C and C−N bonds of the ligands are in the range 0.04−0.015 Å, which actually precludes a meaningful distinction between $(opda)^{2-}$, $(sqdi)^{-}$, and (bqdi) formulations.

We initiated the present work in the hope of obtaining new complexes containing these noninnocent ligands which would give better single crystals and allow thereby a more accurate determination of the C−C and C−N bond lengths and verify the above implications concerning the oxidation state−structure relationship. During the course of this study, we discovered that heating of the solid complex $[LRu^{II}(bqdi)(N_3)](PF_6)$ to 160 °C produces N_2 and a mixed-valent, dinuclear μ-nitrido-bridged species $[\{LRu(o\text{-}C_6H_4(NH)_2)\}_2(\mu\text{-}N)](PF_6)_2$. This complex is electronically interesting because it contains the strong nitrido π-donor *and* two noninnocent chelate ligands.

Experimental Section

Materials. The macrocyclic ligand 1,4,7-trimethyl-1,4,7-triazacyclononane[6] (L) and the starting material $[LRuCl_3]\cdot H_2O$[7] were synthesized as described previously. 1,2-Phenylenediamine was purchased from Aldrich.

Methods. ^1H NMR spectra were recorded on Bruker AM and DRX 400 and DRX 500 instruments at 400.13 and 500.13 MHz, respectively, at 300 K and were referenced to the residual proton signals in deuterated solvents. For high-resolution spectra of the aromatic region of complexes **2** and **4**, a spectral width of 800 Hz was recorded with 16K data points, no line broadening was applied before FT. Folding of unwanted signals into this narrow region was avoided by employing digital filtering and oversampling during data acquisition. The simulation and fitting were carried out using the Bruker program WIN-DAISY on a PC. In all cases, reasonable starting values were obtained from an AA′XX′ simulation of the experimental data. With a constant line width of 1 Hz (obtained from a singlet in the experimental spectrum), the symmetry was then lowered to C_1. The coupling constants and, subsequently, the coupling constants *and* chemical shifts were optimized, and finally, all parameters including the line widths were refined without restraints.

Electronic spectra of complexes in water or acetonitrile solution were recorded on a Perkin-Elmer Lambda 9 UV/vis NIR spectrophotometer in the range 210−1600 nm at ambient temperature.

Cyclic voltammograms were recorded by using PAR equipment (potentiostat 173, universal programmer M 175) at a glassy carbon working electrode. Deaerated acetonitrile solutions of complexes ($\sim 10^{-4}$ M) containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate were scanned (20−200 mV s^{-1}) under an argon blanketing atmosphere. The potentials are referenced to the ferrocenium/ferrocene couple, Fc^+/Fc, throughout.

$[LRu^{II}(bqdi)(OH_2)](PF_6)_2$ (1). A suspension of $[LRu^{III}Cl_3]\cdot H_2O$[7] (0.30 g; 0.79 mmol) and 1,2-phenylenediamine (0.086 g; 0.79 mmol) in water (50 mL) was heated to reflux for 4 h. To the clear, deep red solution was added solid $NaPF_6$ (1.5 g). When the solution was cooled to 5 °C deep red microcrystals precipitated within 24 h. Slow recrystallization from a methanol/water mixture (1:1) produced red crystals of **1** suitable for X-ray crystallography. Yield: 0.48 g (89%). ^1H NMR (400 MHz; CD_3NO_2, 25 °C): δ 1.41 (s, 3H), 1.6 (broad s, H_2O), 2.6−4.0 (m, 12 H), 3.48 (s, 6 H), 6.97 (dd, 2 H), 7.40 (dd, 2 H), 11.58 (s, 2 H). FAB MS: *m/z* 414 ($\{M + H_2O\}^+$), 396 (M^+), 378 ($\{M - H_2O\}^+$). IR (KBr): $\nu(H_2O)$ 3430 b, $\nu(N{-}H)$ 3300 cm^{-1}. Anal. Calcd for $C_{15}H_{29}F_{12}N_5OP_2Ru$: C, 26.2; H, 4.3; N, 10.2. Found: C, 26.4; H, 4.3; N, 10.3.

$[\{LRu^{II}(bqdi)\}_2(\mu\text{-}O_2H_3)](PF_6)_3$ (1a). To a solution of **1** (0.30 g; 0.44 mmol) in methanol (30 mL) was added 0.01 M aqueous NaOH (10 mL). Slow evaporation of the solvent in an open vessel at ambient temperature yielded orange-red crystals of **1a** within a few days. Yield: 0.20 g (74%). ^1H NMR (400 MHz; CD_3NO_2, 25 °C): δ 1.02 (s, 3H), 2.6−3.5 (m, 12 H), 2.95 (s, 6 H), 6.91 (dd, 2 H), 7.30 (dd, 2 H). FAB MS: *m/z* 1082 ($\{M(PF_6)_2\}^+$), 936 ($\{M(PF_6)\}^+$). Anal. Calcd for $C_{30}H_{57}F_{18}N_{10}O_2P_3Ru_2$: C, 29.4; H, 4.7; N, 11.4. Found: C, 29.2; H, 4.9; N, 11.2.

$[LRu^{II}(bqdi)(NCCH_3)](PF_6)_2$ (2). A solution of **1** (0.30 g; 0.44 mmol) in dry CH_3CN (40 mL) to which P_2O_5 (0.10 g) had been added was heated to reflux for 4 h under an Ar blanketing atmosphere. The solvent was removed from the filtered solution by rotary evaporation. The deep red residue was dissolved in methanol (20 mL). The solution was allowed to stand in an open vessel until orange-red microcrystals had precipitated. Yield: 0.21 g (64%). ^1H NMR (400 MHz; CD_3NO_2, 25 °C): δ 1.56 (s, 3H), 2.21 (s, 3 H), 2.8−3.6 (m, 12 H), 3.45 (s, 6 H), 6.92 (dd, 2 H), 7.26 (dd, 2 H), 11.7 (s, 2 H). FAB MS: *m/z* 565 ($\{MPF_6\}^+$), 419 (M^+), 379 ($\{M - CH_3CN\}^+$). Anal. Calcd for $C_{17}H_{30}F_{12}N_6P_2Ru$: C, 28.8; H, 4.3; N, 11.8. Found: C, 28.7; H, 4.6; N, 11.6.

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Table 1. Crystallographic Data for **1**, **1a**·3MeCN, **3**, **4**·H_2O, and **5**·3MeCN·0.5(toluene)

	1	**1a**·3 MeCN	**3**	**4**·H_2O	**5**·3MeCN·0.5(toluene)
formula	$C_{15}H_{29}F_{12}N_5OP_2Ru$	$C_{36}H_{66}F_{18}N_{13}O_2P_3Ru_2$	$C_{15}H_{27}I_2N_5Ru$	$C_{15}H_{29}F_6N_8OPRu$	$C_{39.5}H_{67}F_{12}N_{14}P_2Ru_2$
fw	686.44	1350.07	632.29	583.48	1230.15
space group	$P2_1/m$	$C2/c$	$Pnma$	$P2_1/c$	$P2_1/c$
a, Å	8.412(2)	19.858(3)	18.399(4)	8.586(1)	15.003(3)
b, Å	15.562(3)	15.483(2)	9.287(2)	15.617(3)	16.253(3)
c, Å	10.025(2)	18.192(3)	12.052(2)	16.388(5)	21.196(4)
β, deg	109.89(2)	95.95(2)	90	90.84(2)	96.78(3)
V, Å^3	1234.1(5)	5563.2(11)	2059.3(7)	2197.2(6)	5132(2)
Z	2	4	4	4	4
diffractometer	SYNTEX R3	Enraf-Nonius CAD-4	Siemens P4	SYNTEX R3	Enraf-Nonius CAD-4
ρ_{calcd}, g cm^{-3}	1.847	1.612	2.039	1.76	1.592
no. of data	5702	6544	3174	5238	9295
no. of unique data	3067	6333	3172	4082	7154
no. of params	169	331	109	285	573
μ(Mo Kα), cm^{-1}	8.75	7.34	37.66	8.60	7.39
R1^a	0.0469	0.0578	0.0382	0.0474	0.0590
$R_w{}^a$				0.0469	
wR2^b	0.1179	0.1793	0.0981		0.1975

[a] Observation criterion: $I > 2\sigma(I)$. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ where $w = 4F_o^2/\sigma^2(F_o^2)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

[LRu^{II}(bqdi)I](PF$_6$)·0.5H$_2$O (3). A suspension of [LRuCl$_3$]·H_2O (0.10 g; 0.26 mmol) and 1,2-phenylenediamine (28 mg; 0.26 mmol) in water (10 mL) was heated to reflux for 2 h in the presence of air. A solution of NaI (0.50 g) in water (5 mL) was added, and heating was continued for 30 min. When the mixture was allowed to stand at 5 °C for 24 h, red crystals of [LRu^{II}(bqdi)I]I precipitated, which were collected by filtration and dissolved in an acetone/water mixture (2:1) (20 mL) to which $NaPF_6$ (0.5 g) was added. Upon slow evaporation of the solvent in air, red crystals of **3** were obtained. Yield: 0.13 g (76%). ^{1}H NMR (400 MHz; CD_3CN, 25 °C): δ 1.19 (s, 3H), 2.75−3.6 (m, 12 H), 3.75 (s, 6 H), 6.89 (dd, 2 H), 7.39 (dd, 2 H), 11.46 (s, 2 H). FAB MS: m/z 506 (M$^+$). Anal. Calcd for $C_{15}H_{28}F_6IN_5O_{1/2}PRu$: C, 27.3; H, 4.3; N, 10.6. Found: C, 27.3; H, 4.2; N, 10.3.

[LRu^{II}(bqdi)(N$_3$)](PF$_6$)·H$_2$O (4). A solution of **1** (0.30 g; 0.44 mmol) and NaN_3 (0.60 g; 9.2 mmol) in water (30 mL) was heated to 60 °C for 18 h. Pink microcrystals of **4** precipitated from the cooled solution (5 °C) within a few minutes. Slow recrystallization from an acetone/water mixture (2:1) produced single crystals suitable for X-ray crystallography. Yield: 0.19 g (75%). ^{1}H NMR (400 MHz; CD_3NO_2, 25 °C): δ 1.20 (s, 3H), 2.7−3.6 (m, 12 H), 3.34 (s, 6 H), 6.89 (dd, 2 H), 7.46 (dd, 2 H), 11.3 (s, 2 H). FAB MS: m/z 421 (M$^+$), 393 ({M − N$_2$}$^+$), 379 ({M − N$_3$}$^+$). Anal. Calcd for $C_{15}H_{29}F_6N_8OPRu$: C, 30.8; H, 5.0; N, 19.2. Found: C, 31.0; H, 4.8; N, 19.3.

[{LRu(C$_6$H$_4$(NH)$_2$)}$_2$(μ-N)](PF$_6$)$_2$·3CH$_3$CN·C$_6$H$_5$CH$_3$ (5). Microcrystalline, *in vacuo* predried solid **4** (0.15 g; 0.27 mmol) was transferred into a thoroughly dried vessel which was evacuated by an oil pump. The material was heated *in vacuo* to 160 °C for 30 min, whereupon a color change from red to deep brown was observed. Argon was allowed to diffuse into the cooled evacuated vessel. Under this argon blanketing atmosphere, the brown residue was dissolved in a dry acetonitrile/toluene (1:1) mixture (30 mL). Slow evaporation of the solvent by passing an argon stream through this solution initiated the precipitation of brown crystals of **5**. Yield: 0.11 g (77%). FAB MS: m/z 1061 ({MH(PF$_6$)$_2$}$^+$), 916 ({M(PF$_6$)}$^+$), 770 (M$^+$). Anal. Calcd for $C_{30}H_{54}F_{12}N_{11}P_2Ru_2$: C, 34.0; H, 5.1; N, 14.5. Found: C, 33.8; H, 5.0; N, 14.7.

X-ray Crystallographic Data Collection and Refinement of the Structures. Single crystals of **1**, **1a**, **3**, **4**, and **5** were mounted in capillaries sealed under argon. Graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used throughout. Crystallographic data for the compounds and the diffractometer types used are listed in Table 1. Cell constants were obtained from a least-squares fit of the setting angles of 25 carefully centered reflections in the range $18 < 2\theta < 35°$. The data, collected at 20(1) °C using the $\omega-2\theta$ scan technique, were corrected for Lorentz and polarization effects. No absorption correction was carried out. The Siemens SHELXTL[8] software package was used for solution, refinement, and diagrams of the structures.

All structures were readily solved and refined by direct methods and difference Fourier techniques performed on DEC Alpha workstations. Neutral-atom scattering factors were obtained from ref 9. All non-hydrogen atoms were refined anisotropically except those of the disordered parts of the macrocycle, solvent molecules, and PF_6^- anions, which were isotropically refined by split-atom models. All CH hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Hydrogen atoms bound to oxygen and nitrogen were located from difference Fourier maps and refined isotropically by using temperature factors associated with those of the host atoms.

The ethylene groups in the macrocycles of complexes **1** and **3** showed large apparent displacement parameters leading to unrealistically short C−C distances due to crystallographic mirror planes bisecting the corresponding cations, which results in a static disorder of the methylene carbon atoms. An isotropic split−atom model with a 1:1 occupancy of the carbon atoms C(1), C(2), and C(3) was applied and yielded the expected ($\lambda\lambda\lambda$) and ($\delta\delta\delta$) conformations of the coordinated macrocycle with normal C−C bond distances. Hydrogen atoms of these methylene carbons were attached geometrically with an occupancy factor of 0.5.

The PF_6^- anions in **1a** were found to be disordered. Two of the three anions are located on crystallographic inversion centers, and one lies on a crystallographic 2-fold axis. Only for the latter (F(30), F(31), F(32)) was a split-atom model with an 1:1 occupancy applied. One of the two acetonitrile molecules in the asymmetric unit was also found to be disordered since it is located on a crystallographic inversion center. This disorder was not resolved, and therefore the three non-hydrogen atoms were refined as carbon. The hydrogen atoms of the bridging $(O_2H_3)^-$ group in **1a** were located in the final difference Fourier map and were refined isotropically without restraints.

The cation of compound **4** also showed a slight disorder of the methylene carbons, but splitting of atoms did not improve the refinement. A water molecule of crystallization was found, but attempts to localize the hydrogen atoms failed.

Crystals of **5** contain acetonitrile solvent molecules and toluene. Only one of the acetonitrile molecules was found to be well defined and therefore was refined anisotropically. The other two molecules were refined isotropically with occupancy factors of 0.5 and 0.3, respectively. A 1:1 rigid-body split-atom model was used for the toluene molecule lying near a center of inversion. The methyl group could not be located and therefore was not included in the refinement.

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(8) Software supplied from Siemens Analytical X-ray Instruments, Inc.

(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

Table 2. Electronic and Vibrational Spectra of Complexes

complex	solvent	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	IR (KBr disk), cm^{-1}
1	H_2O (pH = 1)	256 (1.46×10^4), 504 (1.6×10^4), 888 (100)	ν(N−H) 3310; ν(O−H) 3459
1a	H_2O (pH = 12)	260 (8.3×10^4), 494 (1.0×10^4), 875 (60)	ν(N−H) 3322; $\nu(O_2H_3)$ 3489, 3150
2	CH_3CN	245 (2.2×10^4), 509 (1.5×10^4), 830 (180)	ν(N−H) 3301
3	CH_3CN	260 (1.14×10^4), 393 (3.8×10^4), 530 (9.1×10^3), 891 (80)	ν(N−H) 3314; 3217
4	CH_3CN	260 (8.8×10^3), 357 (1.9×10^3), 516 (1.0×10^4), 889 (80)	ν(N−H) 3264; $\nu_{as}(N_3)$ 2037
5	CH_3CN	281 (9.1×10^3), 322 (1.7×10^4), 495 (1.3×10^4), 940 (3.1×10^3)	ν(N−H) 3343

Results

Synthesis. The synthetic routes employed are schematically shown in Scheme 1. Spectroscopic data (UV/vis and IR) for complexes **1**−**5** are given in Table 2.

Complexes containing the LRu fragment are readily prepared by using the starting material $[LRu^{III}Cl_3]\cdot H_2O$.[7] Thus the reaction of this species with 1 equiv of 1,2-phenylenediamine ($opdaH_2$) in water in the presence of air yields a deep red acidic solution from which red diamagnetic crystals of $[LRu^{II}(bqdi)(OH_2)](PF_6)_2$ (**1**) precipitate in 89% yield. Titration of the released protons with aqueous NaOH revealed that 1 equiv of H^+/equiv of $[LRuCl_3]$ is produced according to eq 1. The

$$2[LRu^{III}Cl_3] + 2(opdaH_2) + {}^1/_2O_2 + H_2O \rightarrow 2[LRu^{II}(bqdi)(OH_2)]^{2+} + 6Cl^- + 2H^+ \quad (1)$$

presence of the neutral benzoquinone diimine (bqdi) ligand in **1** which represents the two-electron-oxidized form of $(opda)^{2-}$ is unambiguously established by a single-crystal X-ray structure analysis (see below). In the infrared, a single sharp ν(N−H) vibration is observed at 3300 cm^{-1}, in addition to, a broad ν(OH) mode of the coordinated water molecule at 3459 cm^{-1}.

The pK_a value of the coordinated H_2O in **1** has been determined to be 9.8 in water at 20 °C by potentiometric titration, which may be compared with values of 13.1 for $[Ru^{II}(NH_3)_5(OH_2)]^{2+}$ and 4.2 for $[Ru^{III}(NH_3)_5(OH_2)]^{3+}$.[10] Since (bqdi) is a π-acceptor contrasting, in this respect, the NH_3 ligands, metal-to-ligand charge transfer decreases the electron density at the Ru^{II} ion in **1** and increases the acidity of the $Ru^{II}-OH_2$ moiety somewhat. On the other hand, a pK_a value of 9.8 clearly demonstrates that the central Ru ion does not have an oxidation state of +III (or higher). This is nicely corroborated by the observation that the pK_a of $[LRu^{III}(acac)(OH_2)]^{2+}$, where $acac^-$ represents the redox-innocent ligand pentane-2,4-dionate, is found to be 5.8 at 20 °C.[11]

Orange-red crystals of $[\{LRu(bqdi)\}_2(\mu\text{-}O_2H_3)](PF_6)_3$ (**1a**) precipitated from alkaline methanol/water solutions (pH ∼ 12) of **1**. Complex **1a** is diamagnetic (^{1}H NMR) and contains a dinuclear trication where two LRu^{II}(bqdi) fragments are bridged by an $(O_2H_3)^-$ group. Recrystallization of **1a** from acetonitrile solutions yielded single crystals suitable for X-ray crystallography of $[\{LRu^{II}(bqdi)\}_2(\mu\text{-}O_2H_3)](PF_6)_3\cdot 3CH_3CN$. To the best of our knowledge **1a** represents the first case where the $(O_2H_3)^-$ anion bridges two *divalent* Ru ions.[12] In the analogous structurally characterized species $[\{LRu^{III}(acac)\}_2(\mu\text{-}O_2H_3)](PF_6)_3$, the Ru ions are trivalent.[11]

The coordinated water molecule in **1** is quite labile and is readily displaced by acetonitrile or by monodentate anions such as iodide or azide. Thus red crystalline $[LRu(bqdi)(NCCH_3)](PF_6)_2$ (**2**) was obtained from acetonitrile solutions of **1**. Reaction of **1** with NaI or NaN_3 in water produces, upon addition of $NaPF_6$, red crystals of $[LRu^{II}(bqdi)I](PF_6)\cdot 0.5H_2O$ (**3**) or $[LRu^{II}(bqdi)(N_3)](PF_6)\cdot H_2O$ (**4**), respectively. The reaction of $[LRuCl_3]\cdot H_2O$ with $opdaH_2$ and NaI in H_2O in the presence of air afforded red crystals suitable for X-ray crystallography of [LRu(bqdi)I]I. Complexes **2**−**4** are diamagnetic (^{1}H NMR).

The electronic spectra of complexes **1**−**4** are very similar; in the visible they display a very intense metal-to-ligand charge transfer band ($t_{2g} \rightarrow 3b_1(\pi^*)$) of the Ru(bqdi) fragment in the range 504−530 nm [$\epsilon \sim (1-2) \times 10^4$ L mol^{-1} cm^{-1}] and a d−d transition at 830−890 nm ($\epsilon \sim 10^2$ L mol^{-1} cm^{-1}).[2] In the infrared spectra, in general, a single sharp ν(N−H) stretching mode is observed in the range 3322−3260 cm^{-1} which is assigned to the coordinated (bqdi) ligand. Only in cases where the N−H protons are involved in hydrogen bonding, as in [LRu(bqdi)I]I, is a shift to lower energy and some broadening of the band detected.

The fast atom bombardment mass spectrum (FAB MS) of **4** displays two prominent peaks: one at *m/z* 421 (100%) which corresponds to the molecular ion $[LRu(bqdi)(N_3)]^+$ and, most interestingly, a peak at *m/z* 393 (70%) which is assigned to a nitrido species $[LRu(C_6H_4(NH)_2)(N)]^+$ ($\Delta = 28$, N_2). This is indicative of the fact that, under the experimental conditions of a FAB experiment, **4** is able to split off dinitrogen. Therefore, we have performed a differential thermal analyses (DTA) on solid, carefully predried **4** (in order to remove the water of crystallization prior to this experiment). At 154.8 °C, a single exothermic process is observed. Thermogravimetric experiments revealed that 1.19 + 0.02 equiv of dinitrogen/equiv of **4** is produced, eq 2. The same stoichiometry was found by

$$2[LRu^{II}(bqdi)(N_3)](PF_6) \rightarrow [\{LRu(C_6H_4(NH)_2)\}_2(\mu\text{-}N)](PF_6)_2 + 2.5N_2 \quad (2)$$

measuring the amount of N_2 released manometrically. During these experiments, the color of the solid material changed from pink to brown. Recrystallization of the brown residue from a carefully dried toluene/acetonitrile mixture produced brown crystals of $[\{LRu(C_6H_4(NH)_2)\}_2(\mu\text{-}N)](PF_6)_2\cdot C_6H_5CH_3\cdot 3CH_3CN$ (**5**) which were suitable for X-ray crystallography (see below) in 77% yield. The FAB MS spectrum and elemental analysis are consistent with this formulation of **5** as a dinuclear complex.

Complex **5** is paramagnetic. Temperature-dependent susceptibility measurements (4−300 K) using a SQUID magnetometer revealed a temperature-independent magnetic moment of 1.6μ_B per dinuclear unit. Thus **5** has an $S = {}^1/_2$ ground state as was confirmed by the observation of an isotropic X-band EPR signal at $g = 2.00$ at 10 K for a powdered solid sample of **5**. In the electronic spectrum of **5** measured in CH_3CN solution, a very intense absorption maximum at 940 nm ($\epsilon = 3.1 \times 10^3$) is tentatively assigned to an intervalence charge transfer band since this band is not present in the spectra of any of the complexes **1**−**4**.

From the crystal structure (below) it is clear that two $LRu(C_6H_4(NH)_2)$ fragments are bridged by a nitride (N^{3-}). Complex

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(10) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(11) Schneider, R.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4925.

(12) Ardon, M.; Bino, A. *Structure and Bonding*; Springer-Verlag: Berlin, 1987; Vol. 65.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**, **1a**·3MeCN, **3**, **4**·H_2O, and **5**·3MeCN·0.5(toluene)

		Complex **1**			
Ru(1)−N(1)	2.154(3)	N(3)−Ru(1)−N(3A)	77.3(2)	N(3)−Ru(1)−N(1)	100.19(12)
Ru(1)−N(2)	2.118(4)	N(3)−Ru(1)−N(2)	96.55(12)	N(3A)−Ru(1)−N(1)	177.29(11)
Ru(1)−N(3)	1.998(3)	N(3)−Ru(1)−O(1)	88.01(13)	N(2)−Ru(1)−N(1)	82.60(12)
Ru(1)−O(1)	2.144(4)	N(2)−Ru(1)−O(1)	174.2(2)	O(1)−Ru(1)−N(1)	93.01(13)
		N(1)−Ru(1)−N(1A)	82.3(2)		
		Complex **1a**			
Ru(1)−N(2)	1.981(4)	N(2)−Ru(1)−N(1)	77.6(2)	O(1)−Ru(1)−N(3)	88.2(2)
Ru(1)−N(1)	1.990(4)	N(2)−Ru(1)−O(1)	93.1(2)	N(5)−Ru(1)−N(3)	82.1(2)
Ru(1)−O(1)	2.066(3)	N(1)−Ru(1)−O(1)	90.7(2)	N(2)−Ru(1)−N(4)	99.5(2)
Ru(1)−N(5)	2.104(4)	N(2)−Ru(1)−N(5)	96.6(2)	N(1)−Ru(1)−N(4)	176.5(2)
Ru(1)−N(3)	2.150(4)	N(1)−Ru(1)−N(5)	95.9(2)	O(1)−Ru(1)−N(4)	91.5(2)
Ru(1)−N(4)	2.156(4)	O(1)−Ru(1)−N(5)	169.2(2)	N(5)−Ru(1)−N(4)	82.4(2)
		N(2)−Ru(1)−N(3)	177.7(2)	N(3)−Ru(1)−N(4)	82.3(2)
		N(1)−Ru(1)−N(3)	100.6(2)		
		Complex **3**			
I(1)−Ru(1)	2.732(1)	N(2)−Ru(1)−N(2A)	77.1(2)	N(3)−Ru(1)−N(3A)	81.9(2)
Ru(1)−N(2)	1.991(3)	N(2)−Ru(1)−N(1)	95.19(12)	N(2)−Ru(1)−I(1)	89.37(8)
Ru(1)−N(1)	2.137(4)	N(2)−Ru(1)−N(3)	100.37(14)	N(1)−Ru(1)−I(1)	174.16(12)
Ru(1)−N(3)	2.174(3)	N(2A)−Ru(1)−N(3)	175.63(13)	N(3)−Ru(1)−I(1)	94.19(9)
		N(1)−Ru(1)−N(3)	81.42(13)		
		Complex **4**			
Ru(1)−N(1)	2.145(4)	N(1)−Ru(1)−N(2)	82.3(1)	N(3)−Ru(1)−N(5)	100.3(2)
Ru(1)−N(2)	2.151(4)	N(1)−Ru(1)−N(3)	82.3(2)	N(4)−Ru(1)−N(5)	77.7(2)
Ru(1)−N(3)	2.121(4)	N(2)−Ru(1)−N(3)	82.1(2)	N(1)−Ru(1)−N(6)	88.3(2)
Ru(1)−N(4)	1.983(4)	N(1)−Ru(1)−N(4)	99.9(2)	N(2)−Ru(1)−N(6)	92.4(2)
Ru(1)−N(5)	1.991(4)	N(2)−Ru(1)−N(4)	176.9(2)	N(3)−Ru(1)−N(6)	169.7(2)
Ru(1)−N(6)	2.116(4)	N(3)−Ru(1)−N(4)	96.1(2)	N(4)−Ru(1)−N(6)	89.8(2)
		N(1)−Ru(1)−N(5)	176.6(2)	N(5)−Ru(1)−N(6)	89.2(2)
		N(2)−Ru(1)−N(5)	100.1(2)		
		Complex **5**			
Ru(1)−N(11)	1.767(5)	N(11)−Ru(1)−N(5)	100.5(2)	N(11)−Ru(2)−N(9)	98.0(2)
Ru(1)−N(5)	1.992(5)	N(11)−Ru(1)−N(4)	99.5(2)	N(11)−Ru(2)−N(10)	97.8(2)
Ru(1)−N(4)	1.996(5)	N(5)−Ru(1)−N(4)	78.1(2)	N(9)−Ru(2)−N(10)	77.6(2)
Ru(1)−N(2)	2.171(5)	N(11)−Ru(1)−N(2)	94.5(2)	N(11)−Ru(2)−N(7)	95.0(2)
Ru(1)−N(3)	2.178(6)	N(5)−Ru(1)−N(2)	97.5(2)	N(9)−Ru(2)−N(7)	166.8(2)
Ru(1)−N(1)	2.301(6)	N(4)−Ru(1)−N(2)	165.9(2)	N(10)−Ru(2)−N(7)	98.6(2)
Ru(2)−N(11)	1.802(5)	N(11)−Ru(1)−N(3)	93.4(2)	N(11)−Ru(2)−N(8)	94.0(2)
Ru(2)−N(9)	2.016(5)	N(5)−Ru(1)−N(3)	166.1(2)	N(9)−Ru(2)−N(8)	99.1(2)
Ru(2)−N(10)	2.032(5)	N(4)−Ru(1)−N(3)	99.6(2)	N(10)−Ru(2)−N(8)	168.0(2)
Ru(2)−N(7)	2.162(6)	N(2)−Ru(1)−N(3)	81.4(2)	N(7)−Ru(2)−N(8)	82.0(2)
Ru(2)−N(8)	2.173(6)	N(11)−Ru(1)−N(1)	169.7(2)	N(11)−Ru(2)−N(6)	171.9(2)
Ru(2)−N(6)	2.257(6)	N(5)−Ru(1)−N(1)	87.9(2)	N(9)−Ru(2)−N(6)	87.9(2)
		N(4)−Ru(1)−N(1)	88.0(2)	N(10)−Ru(2)−N(6)	88.8(2)
		N(2)−Ru(1)−N(1)	78.4(2)	N(7)−Ru(2)−N(6)	79.3(2)
		N(3)−Ru(1)−N(1)	78.3(2)	N(8)−Ru(2)−N(6)	79.5(2)

5 is hydrolytically unstable. The reaction with water under an argon atmosphere produces 1 equiv of ammonia, and complex **1** can be reclaimed in ~40% yield from such a solution by addition of $NaPF_6$. Depending on the oxidation level of the noninnocent ligand $[C_6H_4(NH)_2]^{n-}$ ($n = 0, 1, 2$) in **5**, one can, in principle, assign the following formal oxidation number distribution within the mixed-valent dication:

$$[LRu^{IV}(opda)(N)Ru^{V}(opda)L]^{2+}$$

$$[LRu^{IV}(opda)(N)Ru^{IV}(sqdi)L]^{2+}$$

$$[LRu^{III}(sqdi)(N)Ru^{IV}(sqdi)L]^{2+}$$

$$[LRu^{III}(bqdi)(N)Ru^{III}(sqdi)L]^{2+}$$

$$[LRu^{II}(bqdi)(N)Ru^{III}(bqdi)L]^{2+}$$

Crystal Structure Determinations. The crystal structures of **1**, **1a**, **3**, **4**, and **5** were determined by X-ray crystallography. Table 3 summarizes selected bond distances and angles. Figures 1−5 show the structures of the cations in crystals of **1**, **1a**, **3**, **4**, and **5**, respectively.

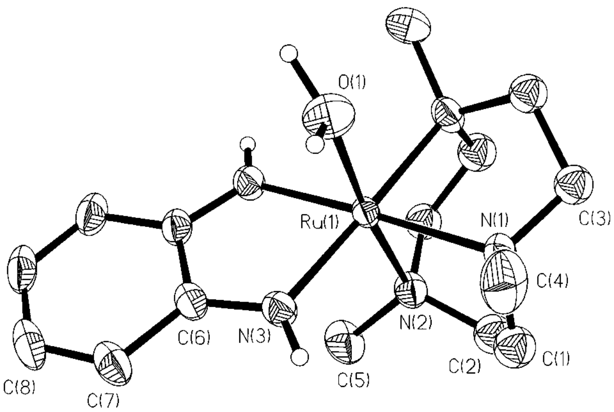

Figure 1. Perspective view of the dication in crystals of **1**. Hydrogen atoms (small open circles) bound to carbon atoms are omitted for the sake of clarity.

We will discuss the structures of the ruthenium(II) complexes **1**, **1a**, **3**, and **4** first, since they all contain an octahedral LRu^{II}(bqdi)X moiety composed of a facially coordinated neutral cyclic triamine L, a bidentate neutral benzoquinone diimine, and a

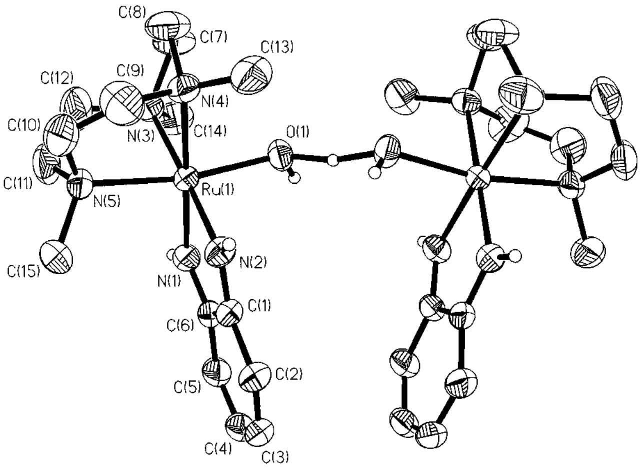

Figure 2. Perspective view of the dinuclear trication in crystals of **1a**. Hydrogen atoms bound to carbon atoms are not shown.

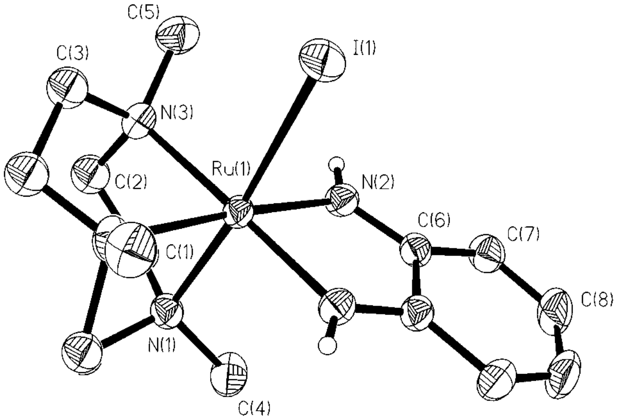

Figure 3. Perspective view of the monocation in crystals of **3**. Hydrogen atoms bound to carbon atoms are not shown.

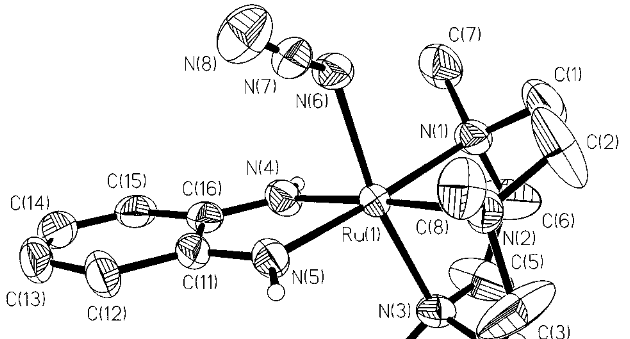

Figure 4. Perspective view of the monocation in crystals of **4**. Hydrogen atoms bound to carbon atoms are not shown.

monodentate ligand, such as a coordinated H_2O in **1**, a bridging $(O_2H_3)^-$ anion in **1a**, an iodide in **3**, and an azide in **4**. The geometrical details of the LRu^{II}(bqdi) fragments in these structures are identical within experimental error. Note that, in all structures, the two protons of the benzoquinone diimine ligand have been unambiguously localized and the nitrogen atoms are sp^2 hybridized.

Figure 6 shows the average bond distances of the N_2Ru^{II}(bqdi) unit in these complexes. Clearly, the bidentate ligand (bqdi) displays predominantly *o*-quinone diimine character with two short C=NH bonds at 1.32 ± 0.01 Å and two short conjugated C=C bonds within the ring at 1.35 + 0.01 Å and three longer C−C single bonds at 1.43 ± 0.01 Å. The same pattern has been reported for $[Ru^{II}(bpy)_2(bqdi)](PF_6)_2$.[4] Interestingly, the two $Ru-N_{(bqdi)}$ bonds are rather short at 1.99 + 0.01 Å and exert a significant trans influence on the $Ru-N_{amine}$ bonds in trans positions (2.16 ± 0.01 Å); the third $Ru-N_{amine}$ bond in a trans position relative to the monodentate ligand X is in all cases shorter at ~2.12 + 0.01 Å.

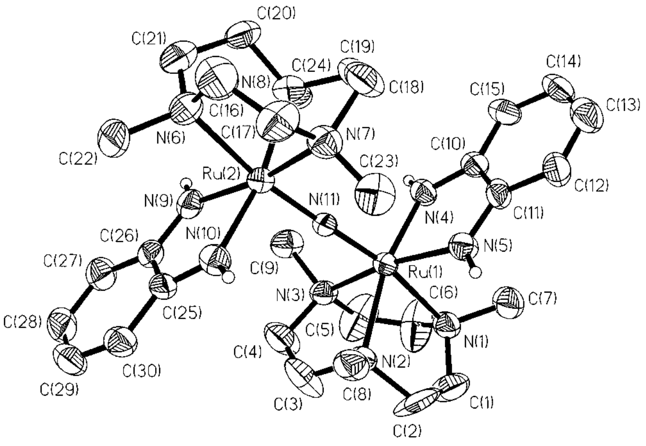

Figure 5. Perspective view of the dinuclear dication in crystals of **5**. Hydrogen atoms bound to carbon atoms are not shown.

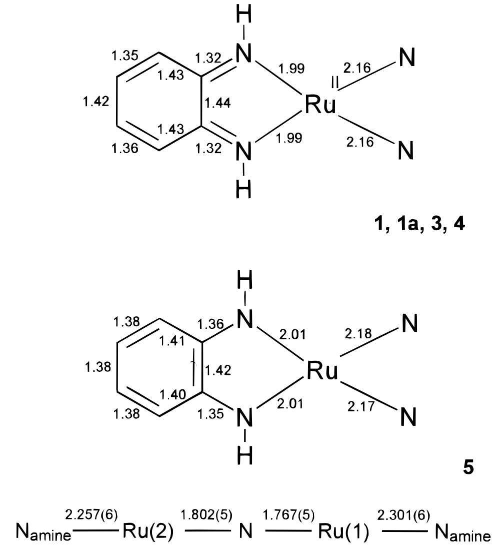

Figure 6. (Top) Average bond distances (Å) in the Ru^{II}(bqdi) fragment of **1**, **1a**, **3**, and **4**. The error is ± 0.01 Å (3σ). (Middle) Average bond distances in the $(C_6H_4(NH)_2)Ru$ fragment in **5**. The error is 0.01 Å. (Bottom) Bond distances of the axis defined by atoms N6−Ru2−N11−Ru1−N1 in the dinuclear dication in **5**.

The LRu(bqdi) fragment possesses idealized C_s symmetry, which in the case of **1** and **3** is crystallographically imposed. Because the three five-membered chelate rings of the coordinated cyclic amine have either ($\lambda\lambda\lambda$) or ($\delta\delta\delta$) conformation, a static disorder of the ethylene carbon atoms is observed in crystals of **1** and **3**. This disorder has been successfully resolved by a split-atom model for these C atoms.

Crystals of **1a** contain a dinuclear trication (Figure 2) where two LRu^{II}(bqdi) fragments are bridged by a $(O_2H_3)^-$ monoanion. The protons of this bridging unit (as well as the N−H protons) have been localized. The trication possesses crystallographically imposed C_2 symmetry. The $(O_2H_3)^-$ bridge also possesses C_2 symmetry with a central proton located on a C_2 axis. The short O···O distance of 2.459(6) Å is indicative of a strong symmetric

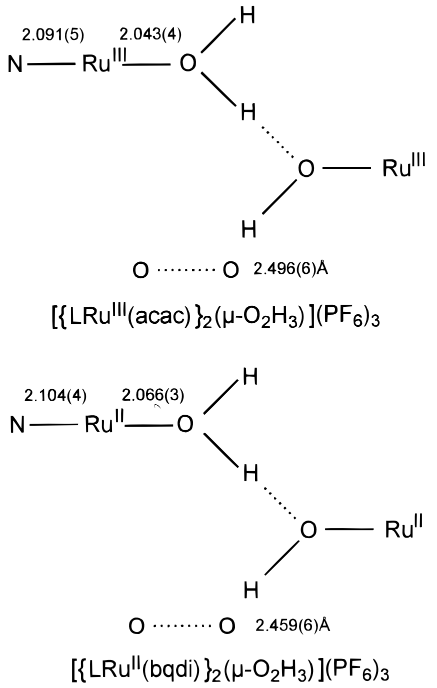

Figure 7. Comparison of the $Ru_2(\mu\text{-}O_2H_3)$ units in $[\{LRu^{III}(acac)\}_2(\mu\text{-}O_2H_3)](PF_6)_3(\mu\text{-}O_2H_3)$ and **1a**.

O-H···O hydrogen-bonding contact.[12] In the corresponding ruthenium(III) complex $[\{LRu^{III}(acac)\}_2(\mu\text{-}O_2H_3)](PF_6)_3$, the bridging (O_2H_3) unit is asymmetric with an O···O distance of 2.494(7) Å (Figure 7). The terminal protons of the $(O_2H_3)^-$ group form a weak N···H-O hydrogen-bonding contact to an acetonitrile molecule of crystallization (N···O 3.042(6) Å) whereas the benzoquinone diimine protons are involved in hydrogen bonds to the PF_6^- anions: F(21)···N(1) 3.203(6), N(2)···F(11) 3.235(6) Å.

Crystals of **5** consist of the dinuclear, μ-nitrido-bridged dication $[\{LRu(C_6H_4(NH)_2)\}_2(\mu\text{-}N)]^{2+}$, PF_6 anions, toluene, and acetonitrile molecules of crystallization. The dication does not possess crystallographically imposed symmetry. It is significant that the nitrido bridge is slightly asymmetric with a comparatively long Ru−N distance (Ru2−N11 1.802(5) Å) and a shorter one (Ru1−N11 1.767(5) Å). Importantly, these two bonds exert a structural trans influence on the respective $Ru-N_{amine}$ bond of differing magnitude (Figure 6). The short $Ru-N_b$ bond weakens the *trans*-$Ru-N_{amine}$ more strongly than the corresponding longer one. The trans influence is defined as the difference Δ between the $Ru-N_{amine}$ bond length in a trans position relative to the nitrido bridge and the average $Ru-N_{amine}$ bond lengths in cis positions. At Ru1, this difference is 0.126 Å whereas, at Ru2, it is 0.090 Å.

The geometrical details of the two ligands $C_6H_5(NH)_2{}^{n-}$ in **5** are identical within experimental error and show considerable *o*-phenylenediamide(2^-) character since all C−C distances within the phenyl rings are very much alike and the C−N bond lengths are longer than those in complexes **1**, **1a**, **3**, and **4**, where the benzoquinone diimine description was found to be the appropriate one. It should be kept in mind that, in Lappert's genuine (*o*-phenylenediamido)tin(II) compounds, the C−N distances have values of 1.38(1) and 1.46(1) Å, approaching even more a genuine C−N single bond.[14]

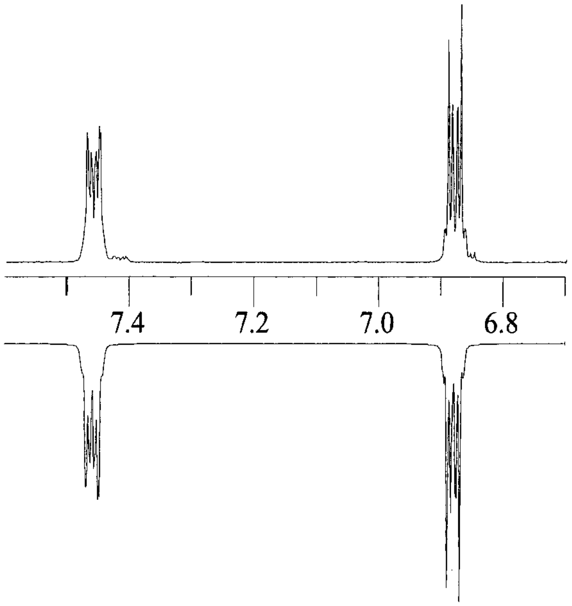

Figure 8. 400 MHz ^1H NMR spectrum of **4** (20 °C, CD_3CN) in the range δ = 6.7−7.5 ppm: upper curve, experimental spectrum; lower curve, simulation with parameters given in Table 4.

If the description as $[C_6H_4(NH)_2]^{2-}$ represents the correct oxidation level of the bidentate ligands in **5**, the dinuclear dication must be described as a $Ru^{IV}Ru^{V}$ mixed-valent species. On the other hand, all structurally characterized nitrido-bridged Ru^{IV}_2 complexes display significantly *shorter* $Ru-N_b$ distances at ∼1.72−1.74 Å.[15] Therefore, we feel that any formalism based on localized oxidation states of metal ions and $[C_6H_4(NH)_2]^{n-}$ ligands does not yield a satisfactory description of the dication in **5**.

^{1}H NMR Spectra of 2 and 4. Hursthouse, Wilkinson, and co-workers[5] have attempted to correlate $^1H-^1H$ coupling constants of the ring protons in $(opda)^{2-}$ of the rhenium complex $[Re^{VII}(opda)_3][ReO_4]$ with the oxidation level of the ligand. Because complexes **1**−**4** contain the (bqdi) form, it appeared to be worthwhile to measure the ^1H NMR spectra of some of these compounds. We have obtained the 400 and 500 MHz spectra of **2** and **4**. Both spectra show a broad signal at ∼12 ppm, which is assigned to the N−H protons, and six multiplets and two singlets between 3 and 4 ppm due to the 12 methylene protons of the macrocyclic triamine and the three methyl groups (see Experimental Section).

In addition, there are two groups of signals at 6.5−8.0 ppm that display to a first approximation the pattern of an AA′XX′ spin system of the $C_6H_4(NH)_2$ moiety. Closer inspection reveals that there are differences between the two groups of signals, and no satisfying simulation was achieved in C_s symmetry. This is an unexpected feature since this asymmetry of the ring proton signals can only be due to the chirality of the coordinated macrocycle L, where the three five-membered chelate rings $\overbrace{Ru-N-C-C-N}$ adopt either (λλλ) or (δδδ) conformation.

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[12]

[13] Another example is *trans*-$[Ru^{III}(bpy)_2(OH)(OH_2)](ClO_4)_2$: Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

[14] (a) Braunschweig, H.; Gerhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1922. (b) Gerhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931.

[15] The average $Ru-N_{nitrido}$ bond length is 1.72 Å in $K_3[Ru^{IV}_2(\mu\text{-}N)Cl_8(H_2O)_2]$, 1.74 Å in $[Ru^{IV}_2(\mu\text{-}N)(en)_5]Cl_5$, and 1.735 Å in $(H_5O_2)[Ru^{IV}_2(\mu\text{-}N)(bpy)_2Cl_6]$: (a) Chiechanowiciz, M.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1969**, 574. (b) Griffith, W. P.; McManus, N. T.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1984**, 434. (c) Haukka, M.; Venäläinen, T.; Ahlgren, M.; Pakkanen, T. A. *Inorg. Chem.* **1995**, *34*, 2931.

Table 4. ^{1}H NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for the Chelating $[C_6H_4(NH)_2]^{n-}$ Ligand in Complexes

complex	J_{AX}	J_{BY}	J_{XY}	J_{AY}	J_{BX}	J_{AB}	δ_A	δ_B	δ_X	δ_Y	ref
2[a]	8.6	8.8	4.5	1.4	1.8	1.6	7.27	7.28	6.92	6.92	this work
4[a]	9.1	8.9	6.5	1.1	1.0	0.7	7.46	7.46	6.88	6.88	this work
$[Re^{VII}(opda)_3]^+$ [b]	8.25		6.36	1.10			7.44		7.03		5
benzotriazole[b,c]	8.3		6.7	1.4							*e*
2-methylbenzotriazole[b,d]	9.4		3.6	0.5							*e*

[a] For proton labels for **2** and **4**, see drawings below. [b] In C_s symmetry: $J_{AX} = J_{BY} = J_A$; $J_{XY} = J_X$; $J_{AY} = J_{BX} = J_{AY}$. [c,d] See drawings below. [e] *Comprehensive Heterocyclic Chemistry*; Katritsky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, U.K., 1984; Vol. 5, Section 15.

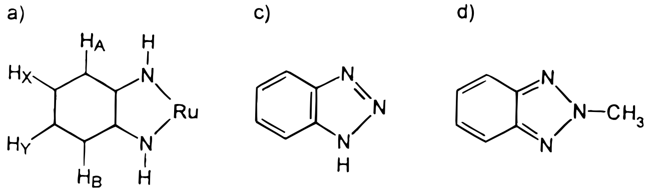

Table 5. Electrochemical Data for the Complexes[a]

	solvent	E,[b] V *vs* Fc$^+$/Fc
2	CH_3CN	+0.84 (r), −1.02 (r), −1.80 (r)
3	CH_3CN	+0.37 (r), −1.31 (irr)
4	CH_3CN	+0.17 (r), −1.33 (r), −2.31 (irr)
5	$(CH_3)_2CO$	−0.35 (irr)

[a] Conditions: glassy carbon working electrode; 0.10 M $[(n\text{-}Bu)_4N]PF_6$ supporting electrolyte; scan rate 100 mV s^{-1}. [b] For reversible (r) processes the redox potentials $E_{1/2} = (E_p^{red} + E_p^{ox})/2$ are given, and for irreversible (irr) processes the peak potentials E_p^{red} are given.

Thus, a good fit of the calculated NMR parameters to the experimental spectra was obtained only by taking into account an ABXY spin system with four different chemical shifts and six coupling constants. The results are listed in Table 4; Figure 8 shows the observed and calculated spectrum of **4** in the range 6.8−7.5 ppm.

At this point, an unusual line width of about 2 Hz is apparent for the low-field multiplet which is to be compared with the expected line width of 1 Hz for the other multiplet. A small coupling on the outer two signals of the low-field multiplet is barely detectable. A 2D COSY experiment unambiguously confirmed a coupling to the N−H protons. A cross-peak between the N−H protons and the multiplet at ~7.45 ppm in the NOESY spectrum of **4** clearly indicates spatial proximity. Therefore, the small coupling is due to $^4J_{HH}$ coupling. Adding a coupling constant of ~1 Hz to the simulation results in the excellent fit shown in Figure 8, and the line width of all signals is now close to 1 Hz, which is the experimental resolution. The same coupling was detected in the spectrum of **2**.

Inspection of the data in Table 4 reveals that it is difficult (if not impossible) to discern conclusively, from the observed ^{1}H−^{1}H coupling constants, between a coordinated *o*-phenylenediamide as has been suggested to be present in $[Re^{VII}(opda)_3]^+$ and a benzoquinone diimine as in complexes **1**−**4** because the coupling constants are very similar. Note that the (bqdi) formulation in **1**−**4** is supported by the present structure determinations whereas, for $[Re^{VII}(opda)_3][ReO_4]$, the $(opda)^{2-}$ formulation is structurally less firmly established (very large esd values for C−C and C−N bonds).

Electrochemistry. Cyclic voltammograms (CV's) of complexes **2**−**5** have been recorded in acetonitrile (or acetone **5**) solution containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate. The potentials are referenced to the ferrocenium/ferrocene (Fc$^+$/Fc) couple. The results are summarized in Table 5.

The CV of **2** displays three reversible (ΔE_p = 75−80 mV) one-electron transfer processes at +0.84, −1.02, and −1.80 V, respectively. We assign the first wave to the metal-centered Ru^{III}/Ru^{II} couple. Remarkably, substitution of the (bqdi)ligand in **2** by pentane-2,4-dionate(1$^-$) (acac), affording $[LRu(acac)(CH_3CN)]^+$, shifts the redox potential for the Ru^{III}/Ru^{II} couple by 0.99 V cathodically ($E_{1/2}$ = −0.15 V).[11] This is clear evidence for the enormous stabilization of the divalent Ru center by the π-acceptor (bqdi) as compared to (acac)$^-$. It is noted that the acetonitrile ligand is also a good π-acceptor: The ν(C≡N) stretching frequency of **2** is observed at 2287 cm^{-1} whereas, for $[LRu(acac)(CH_3CN)]^+$, it is at 2242 cm^{-1}, where the CH_3CN ligand is the only π-accepting ligand present.

The other two reduction waves of **2** are probably ligand-centered and correspond to the reversible formation of coordinated (sqdi)$^-$ and (opda)$^{2-}$ ligands (eq 3). Similarly, complexes

$$[LRu^{II}(bqdi)(CH_3CN)]^{2+} \underset{-e}{\overset{+e}{\rightleftharpoons}} [LRu^{II}(sqdi)(CH_3CN)]^{+} \underset{-e}{\overset{+e}{\rightleftharpoons}} [LRu^{II}(opda)(CH_3CN)]^{0} \quad (3)$$

3 and **4** each display a reversible metal-centered one-electron transfer wave at a less positive redox potential than **2**, whereas the first ligand-centered reduction is reversible for **4** but irreversible for **3** and the second ligand reduction was detected as an irreversible process only for **4**.

Complex **5** cannot be oxidized up to +1.5 V but is irreversibly reduced at a peak potential E_p^{red} = −0.35 V *vs* Fc$^+$/Fc. It is not clear if this process is ligand- or metal-centered.

Discussion

The crystallographic data for complexes **1**−**4** strongly support the notion that the bidentate chelating ligand $(C_6H_4(NH)_2)$ is bound as neutral benzoquinone diimine. Consequently, the central ruthenium(II) ion has a d^6 low-spin electron configuration. The electrochemistry of **2**−**4** displaying at negative potentials two one-electron reduction waves (in one instance, namely **2**) is in accord with ligand-centered processes yielding (opda)$^{2-}$ ligands. It is also noted that the ν(N−H) stretching mode for complexes where the N−H protons are not involved in strong hydrogen-bonding contacts is observed as a single sharp band at ~3300 cm^{-1} whereas, for **5**, this mode is shifted to *higher* energy at 3343 cm^{-1}. This is in accord with the interpretation that the bidentate ligands in **5** have some (opda)$^{2-}$ character, which also agrees with the structure determination.

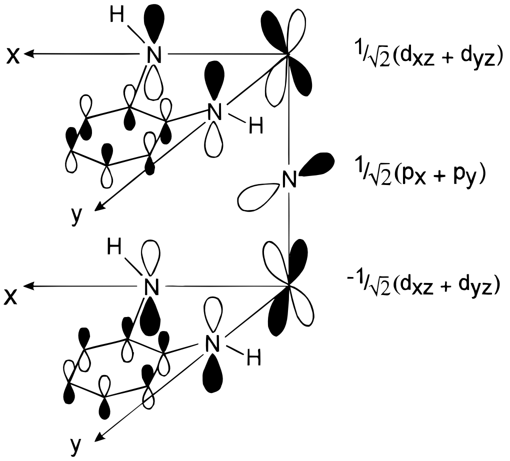

Figure 9. Orbital interactions between a p orbital of the N^{3-} bridge and two d orbitals of the Ru ions and the $3b_1(\pi^*)$ orbitals of the two $C_6H_4(NH)_2$ ligands which, for the sake of clarity, are oriented in cis positions relative to each other (the same scheme holds with these ligands in trans position).

On the other hand, the fact that the Ru−N−Ru unit in **5** is not quite symmetric and both Ru−N bonds are longer than the corresponding bonds in all known and crystallographically characterized genuine Ru^{IV}═N═Ru^{IV} species indicates to us that a description of **5** as $[LRu^{IV}(opda)(\mu\text{-}N)Ru^{V}(opda)L]^{2+}$ is not appropriate. The chemical reactivity of **5** (ready hydrolysis yielding NH_3) also points to an electron-rich nitrido bridge in **5**, where π-donation to an electron-poor Ru^{IV} and Ru^{V} center is not fully developed.

In conclusion, it appears not to be possible to describe the electronic structure of the dication in **5** by using localized valencies for the ruthenium ions and the bidentate ligands. The π-donor N^{3-} and the π-acceptor $C_6H_4(NH)_2$ ligand orbitals probably have energies similar to those of the metal d orbitals of the t_{2g} subshell (in O_h symmetry), and a molecular orbital description as shown in Figure 9 is best suited to describe the bonding in **5**.

Figure 9 shows the symmetry- adapted t_{2g} orbitals on each ruthenium which overlap with both nitride π orbitals and $C_6H_4(NH)_2$ frontier orbitals. Depending on the assignments of oxidation states, this interaction can be viewed either as a synergy between the π-donor N^{3-} and the π-acceptor (bqdi) in which case the ligand orbital $3b_1$ is the LUMO or as a competition between the two π-donors N^{3-} and $opda^{2-}$. In the latter case, the ligand orbital $3b_1$ is the HOMO. This interaction would, in principle, be strengthened by an empty t_{2g} metal orbital (high-valent Ru center). Note that only one nitride π orbital can interact with the $C_6H_4(NH)_2$ frontier orbitals.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support of this work.

Supporting Information Available: Complete lists of atomic positions and *U* values, bond lengths and angles, anisotropic thermal displacement parameters, hydrogen atom coordinates, and data collection and crystal parameters for **1**, **1a**, **3**, **4**, and **5** (31 pages). Ordering information is given on any current masthead page.

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